Answer to the comment of Chudnovsky: On the square-root time relaxation in molecular nanomagnets

(February 1, 2008)

In Ref. [1],we presented a new technique, which we call the *hole digging* method that can be used to observe the time evolution of molecular states in crystals of molecular clusters. It allows us to measure the statistical distribution of magnetic bias fields that arise from the weak dipole fields of the clusters themselves. A hole can be 'dug' into the distribution by depleting the available spins at a given applied field. Our method is based on the simple idea that after a rapid field change, the resulting short time relaxation of the magnetization is directly related to the number of molecules which are in resonance at the given applied field.

Prokof'ev and Stamp have suggested that the short time relaxation should follow a $\sqrt{t}-$relaxation law [2]. However, the hole digging method should work with any short time relaxation law [3]. For the molecular cluster system Fe_8 it is an experimental fact that the short time relaxation follows to a good approximation the $\sqrt{t}-$relaxation law, regardless whether we start from the saturation magnetization [4], or from an annealed state [1,5]. This is true as long as the measurements are made below 400 mK, and therefore the relaxation is purely due to quantum tunneling, and not to thermal activation [6].

An important result of our paper was the observation that the hole line width becomes independent of the initial value of the magnetization for small values of the later. We suggested in Ref. [1] that this *intrinsic* hole line width is directly related to the inhomogeneous level broadening due to nuclear spins as predicted by Prokof'ev and Stamp. Since the publication of our article, we have made new measurements on isotopically substituted samples of Fe_8. Samples enriched with ^{57}Fe had a larger hole line width, and samples where H is replaced with deuterium had a more narrow hole line width [7]. These measurements confirm our hypotheses, and are in quantitative agreement which numerical simulations which takes into account the altered hyperfine coupling [7].

For a *saturated* sample, the Prokof'ev–Stamp theory allows us to estimate the tunneling matrix element Δ. Using Eqs. (3), (9) and (12) of [2], and integration, we find $\int \Gamma_{\rm sqrt} d\xi = c\frac{\xi_0}{E_D}\frac{\Delta^2}{\hbar}$, where c is a constant of the order of unity which depends on the sample shape. With $E_D = 15$ mT, $\xi_0 = 0.8$ mT, $c = 1$ and $\Gamma_{\rm sqrt}$ from Fig. 3 in [1], we find $\Delta = 0.6 \times 10^{-7}$ K which is close to the result of $\Delta = 0.5 \times 10^{-7}$ K obtained by using a Landau Zener method [8].

As for Mn_{12} in Ref [9] we did *not* claim that the relaxation follows the $\sqrt{t}-$ relaxation law. It is well known that the situation in this sample is more complicated due to the fact that there are several coexisting species of Mn_{12} in any crystal, each with different relaxation times. In Ref [9] we were able to isolate one faster relaxing species and we stated in that case, that the relaxation can be *approximately* fit to the $\sqrt{t}-$ relaxation law, but in fact is better fit to a power law t^α with $0.3 < \alpha < 0.5$ (depending on the applied field). We applied the hole digging method to this species, and found evidence for intrinsic line broadening below 0.3K which we suggest comes from nuclear spins in analogy with Fe_8. It should be mentioned that a constant external field can only shift the internal fields. We also measured the relaxation of Mn_{12} at higher temperature (0.04 - 5 K) and found *no evidence what so ever* for a short time $\sqrt{t}-$ relaxation.

Finally, we emphasize that the measurements of short time relaxation allows us to study the time evolution of a well-defined initial state, whereas the interpretation of long time relaxation data are far more difficult due to the development of complex intermolecular correlations during the relaxation process, which are not yet well understood [2,4].

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[3] For example a power law $M \sim (\Gamma_{short} t)^\alpha$, where Γ_{short} is a characteristic short time relaxation rate.

[4] T. Ohm, C. Sangregorio, C. Paulsen, Euro. Phys. J. B **6**, 195 (1998); T. Ohm, C. Sangregorio, C. Paulsen, J. Low Temp. Phys. **113**, 1141 (1998).

[5] For thermal annealed samples, we found experimentally that the smaller the difference $(M_{eq} - M_{in})$, the better is the $\sqrt{t}-$fit.

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[8] W.Wernsdorfer and R. Sessoli, Science **284**, 133 (1999). In this paper, Δ is the tunnel spitting which is two times the tunneling matrix element which was used in [1].

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